IX. *On Benzoline, a new Organic Salt-base from Bitter Almond Oil.*

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WHEN pure oil of bitter almonds is left some days in contact with a strong solution of ammonia, at the ordinary temperature of the air, it is slowly, but in the end completely converted into a white crystalline substance, insoluble in water, but readily soluble in hot alcohol. The solidification of the oil is complete, and there is no secondary product. This substance was examined by M. LAURENT*, who conferred upon it the name of *hydrobenzamide*, and assigned to it the formula $C_{42}H_{18}N_2$; it is generated by the union of the elements of two equivalents of ammonia with those of three equivalents of hydruret of benzoyle, and the separation of six equivalents of water.

3 eq. bitter almond oil .	$C_{42}H_{18}O_6$	Hydrobenzamide	$C_{42}H_{18}N_2$
2 eq. ammonia.	H_6N_2	6 eq. water . . .	H_6O_6
	$C_{42}H_{24}N_2O_6$		$C_{42}H_{24}N_2O_6$

Acids decompose hydrobenzamide immediately, with separation of bitter almond oil and formation of salt of ammonia; with alkalies the case is different, solution of potash, even at a boiling heat, occasioning, as remarked by M. LAURENT, no perceptible change. I found however that when the boiling was prolonged for some hours, a change was induced resembling that undergone by *furfurolamide*† under similar circumstances. A few brownish crystalline flocks appear in the solution, and after cooling, the cake of resin-like substance is found harder and less fusible than hydrobenzamide which has been melted and left to solidify. This change is unaccompanied by any notable alteration of weight, although a faint odour of bitter almond oil is disengaged during the whole course of the ebullition. The new substance is an organic salt-base, having the same composition as hydrobenzamide itself; it might perhaps with propriety be called *benzoline*.

The salts formed by this substance are for the most part remarkable for sparing solubility, with the exception of the acetate; the hydrochlorate, the nitrate, and the sulphate are crystallizable; the last-named salt is exceedingly beautiful, crystallizing from an acid solution in colourless prisms resembling those of oxalic acid.

Precipitated by ammonia from a cold solution of the hydrochlorate or sulphate,

* Ann. Chim. et Phys. 62, p. 23.

† See preceding paper.

benzoline separates in white curdy masses, which when washed and dried diminished greatly in volume; when quite dry the powder is singularly electric; if rubbed with a spatula its particles repel each other with violence, scattering the powder over the paper on which it lies. It is not sensibly soluble in water, but dissolves with great ease in alcohol and ether. A hot alcoholic solution left for some time deposits the base in brilliant transparent colourless crystals, which apparently have the form of square prisms with variously-terminated summits; the alcoholic solution is strongly alkaline to test-paper. At a temperature below 212° benzoline melts, and on cooling assumes a transparent glassy state, without any tendency to crystallization. Heated in a retort, it boils and at length entirely volatilizes, with scarcely a residue of charcoal. Ammonia is disengaged during the distillation, a highly volatile oily liquid, having the odour of benzine, collects in the receiver, and a crystalline solid matter condenses in the neck of the retort. This latter substance, which seems to be the most abundant product, has been but partially examined; it is described below under the name *pyrobenzoline*.

The action of oxidizing agents upon benzoline is remarkable. When heated in a retort with a mixture of bichromate of potash, sulphuric acid and water, it is attacked with great energy, the mixture becomes dark green, and on distillation benzoic acid in large quantity passes over with the vapour of water. With nitric acid the same change seems to occur, but the action is not so definite and speedy. Hydrobenzamide, under similar circumstances, yields the same product, accompanied however in the first part of the distillation by a little bitter almond oil. Melted hydrate of potash appears to exert no action on benzoline, unless the temperature be excessive.

The composition of this substance and its isomerism with hydrobenzamide, are shown by the following analyses:—

	(1.)	(2.)	(3.)
Substance	4·018 grs.	4·03 grs.	4·57 grs.
Carbonic acid produced . .	12·37 grs.	12·46 grs.	14·14 grs.
Water produced	2·21 grs.	2·18 grs.	2·52 grs.

In 100 parts,—

	(1.)	(2.)	(3.)
Carbon . . .	83·96	84·32	84·38
Hydrogen . .	6·11	6·01	6·12

The nitrogen was determined by the process of MM. Will and Varrentrapp, as below:—

	(1.)	(2.)
Substance.	3·88 grs.	5·036 grs.
Platinum salt produced . . .	5·57 grs.	7·28 grs.
Per-centage of nitrogen . . .	9·07	9·12

Hydrobenzamide contains by calculation in 100 parts,—

Carbon	84·56
Hydrogen	6·04
Nitrogen	9·40
	100·00

Hydrochlorate.—The hydrochlorate of benzoline is a sparingly-soluble salt even in boiling water. It crystallizes from a hot solution in small but exceedingly brilliant colourless needles, which effloresce in the dry vacuum. It has, in common with the other salts, an intensely bitter taste. The salt, deprived of its water of crystallization, gave the following analytical results:—

	(1.)	(2.)
Substance	4·25 grs.	4·458 grs.
Carbonic acid produced	11·71 grs.	12·30 grs.
Water produced . . .	2·21 grs.	2·32 grs.

In 100 parts,—

	(1.)	(2.)
Carbon	75·14	75·25
Hydrogen	5·77	5·78

Estimation of nitrogen and chlorine:—

Substance	4·16 grs.
Platinum salt produced . . .	5·17 grs.
Per-centage of nitrogen . . .	7·83

	(1.)	(2.)
Substance	5·838 grs.	4·218 grs.
Chloride of silver produced	2·32 grs.	1·76 grs.
Per-centage of chlorine .	9·64	10·12

The formula $C_{42}H_{18}N_2$, HCl gives in 100 parts,—

Carbon	75·33
Hydrogen	5·68
Nitrogen	8·41
Chlorine	10·58
	100·00

The crystallized salt was found to lose by efflorescence 2·4 per cent. of water, corresponding very nearly to one equivalent.

The hydrochlorate of benzoline forms with bichloride of platinum an insoluble double salt of a pale yellow colour, not further examined.

Nitrate.—The nitrate is even less soluble than the preceding salt; the crystals are

small and have but little brilliancy; they are permanent in the dry vacuum. A portion subjected to analysis gave the following results :—

	(1.)	(2.)
Substance	4·112 grs.	4·27 grs.
Carbonic acid produced	10·51 grs.	10·91 grs.
Water produced . . .	1·97 grs.	2·03 grs.

In 100 parts,—

	(1.)	(2.)
Carbon	69·71	69·68
Hydrogen	5·32	5·28

The formula $C_{42}H_{18}N_2, NO_5+HO$, gives in 100 parts,—

Carbon	69·77
Hydrogen	5·26

The *acetate* is a very soluble salt; it dries up, on evaporation, to a gummy adhesive mass, and probably crystallizes with difficulty, if at all.

Pyrobenzoline.—This, as before observed, is the solid product of the dry distillation of benzoline. It is pressed between folds of bibulous paper to free it as much as possible from oily matter, and then crystallized from boiling alcohol, in which it dissolves pretty freely. It is but sparingly soluble in alcohol in the cold, and apparently quite insoluble in water, dilute acids and alkalies. It is tasteless, and the alcoholic solution has little or no alkaline reaction. At a high temperature this substance fuses, and with still further increase of heat distils; it sublimes at a temperature below its boiling-point, the vapour condensing in feathery crystals like those of benzoic acid. Melted pyrobenzoline on cooling forms a mass of radiated crystals, presenting a great contrast to the glassy or resinous appearance of benzoline under similar circumstances. This substance was at first imagined to be a hydrocarbon; it contains nitrogen, however, and gave on analysis the results stated below.

	(1.)	(2.)
Substance	4·295 grs.	3·46 grs.
Carbonic acid produced	13·42 grs.	10·74 grs.
Water produced . . .	2·08 grs.	1·71 grs.

Hence in 100 parts,—

	(1.)	(2.)
Carbon	85·21	84·66
Hydrogen	5·38	5·49

Estimation of nitrogen :—

Substance	4·15 grs.
Platinum salt produced . . .	6·00 grs.
Per-centage of nitrogen . . .	9·11

These numbers lead to the formula $C_{21} H_8 N$, which gives in 100 parts,—

Carbon	85·1
Hydrogen	5·4
Nitrogen	9·5
	100·00

This, which appears to be a neutral body, together with its accompanying liquid product, deserves a more extended examination.

The hope which I ventured to express in a former paper of the formation of new organic bases from the volatile oils which unite with ammonia, by subjecting their *amides* to the influence of agents, as caustic potash, capable of bringing about metamorphosis of the compound into a more stable form or forms of combination, has thus been partially fulfilled.

M. Laurent has recently announced the discovery of a new substance obtained from bitter almond oil, isomeric with hydrobenzamide, possessing basic properties, and corresponding in some other respects with benzoline; it is stated however to be volatile without decomposition, which is certainly not the case with that body. The name *amarine* was conferred upon it*. The publication of the experiments in detail will probably determine the identity or separate nature of the two substances.

* Comptes Rendus, xix. p. 353.

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